Formation of a Bimolecular First Layer in *tert*-Butanol on Graphite

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We report here the pressure-volume isotherm and x-ray diffraction measurements for *tert*-butanol on graphite over the temperature range of 220–250 K, with comparison to the other branched isomers of butanol. Unlike the other butanols, the first adsorbed layer of *tert*-butanol forms a bimolecular-layer-thick film and undergoes two first-order phase transitions with increasing vapor pressure. Analysis of the x-ray diffraction pattern shows that the bimolecular adsorbed layer shares the same helical structure of hydrogen bonds as found in the bulk.

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Adsorption isotherms of simple gases on a uniform substrate surface usually show a series of steps having comparable height, which indicate layer by layer growth of successive monomolecular layers with increasing vapor pressure [1]. This results from the fact that the attractive interactions between the substrate and the molecule decrease discontinuously with increasing layer number. If the molecule-substrate interactions are comparable to the molecule-molecule interactions, or the adsorbed layer is strongly strained, the thickness of the multilayer coexisting with the bulk is limited to a few layers [2]. In any case, the first adsorbed layers always form monomolecular-layer-thick films in all the systems examined so far. In addition, the adsorption isotherms often show successive phase transitions within the first adsorbed monolayer [1]. A vast number of studies have been devoted to the problem of elucidating the structure and phase transitions of these monolayer films [3]. In the course of the systematic study of alcohols adsorbed on graphite, we found that the first adsorbed layer of *tert*-butanol forms a bimolecular-layer-thick film and undergoes two first-order phase transitions with increasing vapor pressure. In contrast to the adsorption of gases on a solid surface, formation of the bimolecular-layer structure is well established in biolipids [4] and synthetic amphiphiles [5] dispersed in water, as well as soap black films [6].

In this Letter we report the pressure-volume isotherms and x-ray diffraction results of *tert*-butanol adsorbed on exfoliated graphite which is a well-known adsorbant with a high surface uniformity [1]. As far as we know, this is the first observation concerning the formation of a bimolecular first layer in gas molecules on a solid substrate. We will give some evidence to support this finding.

The adsorption isotherm was measured volumetrically on 0.1 g of noncompressed exfoliated graphite using a greaseless system constructed of metal valves, stainless-steel tubes, and a glass sample cell. The pressure was measured by a Baratron capacitance manometer (type 310-BH) with a full scale of 1 Torr. The adsorption temperature was regulated to within ±0.1 K with an Oxford temperature controller (model DTC2) having a Pt sensor. The substrate was repeatedly evacuated at 623 K under a vacuum of 1×10^{-5} Torr for 5 h, prior to adsorption. Alcohols were purified by vacuum distillation and then stored over dehydrated 3-Å molecular sieves. The experimental apparatus and procedures of x-ray diffraction have been described in detail elsewhere [7]. Cu $K\alpha$ radiation was used in the experiment. The substrate used in the diffraction study was the recompressed exfoliated graphite, Grafoil. The surface areas of both substrates were determined from the adsorbed amount at the commensurate-incommensurate transition of Kr by assuming the cross section of Kr to be 0.1572 nm^2 [1].

We measured the adsorption isotherms of methanol, ethanol, *n*-propanol, 2-propanol, *n*-butanol, *sec*-butanol, isobutanol, *tert*-butanol, and neopentane in the temperature ranges of 207.9–228.0, 219.1–239.8, 234.0–254.6, 228.0–249.5, 249.5–270.1, 234.7–255.3, 239.9–260.5, 227.5–253.3, and 167.8–180.1 K, respectively, on the ex-

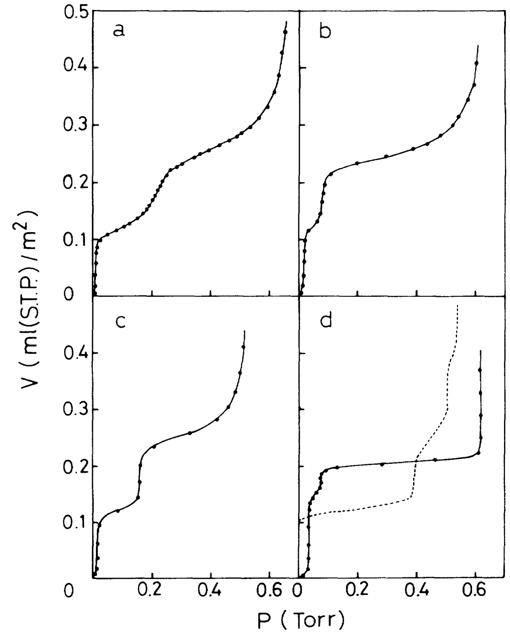

FIG. 1. Adsorption isotherms of butanols on graphite: (a) *n*-butanol at 270.1 K, (b) *sec*-butanol at 255.3 K, (c) isobutanol at 260.5 K, and (d) *tert*-butanol at 250.7 K. Dotted line in (d) represents the adsorption isotherm of neopentane at 177.0 K.

foliated graphite. Figure 1 shows selected isotherms of *n*-butanol, *sec*-butanol, isobutanol, *tert*-butanol, and neopentane. The adsorption isotherm of neopentane gives a clear-cut example of a stepwise isotherm, which indicates the high uniformity of the substrate surface used in the present experiment. Adsorptions of ethanol, *n*-propanol, 2-propanol, *n*-butanol, *sec*-butanol, and isobutanol resulted in stepwise isotherms having only two steps of comparable height, and an adsorption of methanol gave S-shaped isotherms with only one step. The shape of all these isotherms did not appreciably change with temperature within the temperature regions examined here. On the other hand, the shape of the isotherms of *tert*-butanol changed remarkably with temperature. The isotherm at a higher temperature is given in this figure. It shows two steps of different heights before reaching the saturated vapor pressure of 0.6 Torr. When the temperature is lowered, these two steps merge into one step. Evidently, these two steps in *tert*-butanol do not indicate the successive growth of monomolecular layers, unlike the steps of the other alcohols, although the adsorbed amount after the formation of the substep in *tert*-butanol is comparable to those after the formation of the second steps in neopentane having an analogous molecular structure and in the other branched isomers of butanol.

A set of isotherms of *tert*-butanol on the exfoliated graphite are presented in Fig. 2. Their general appearance is similar to that of xenon [1] on the same substrate within the first adsorbed layer. They show that the first adsorbed layer undergoes two first-order phase transitions above 232.7 K. When the temperature is lowered, the two steps approach and eventually merge into one large step at 230.1 K. Just before merging, the height of the first step decreases markedly with decreasing temperature, while that of the second step has a corresponding increase. The adsorbed amount after the formation of the first step at higher temperatures already exceeds the saturated amounts of the first adsorbed layer in neopentane and in the other butanols. From the analogy to the Xe/graphite system [1], the first and second steps at higher temperatures may be ascribed to two-dimensional (2D) gas-liquid and liquid-solid transitions, respectively.

TABLE I. Saturated amounts of the first adsorbed layer in various alcohols on graphite.

	[ml(STP)/m^2]	(molecules/nm^2)
Methanol	0.236	6.34
Ethanol	0.183	4.92
n-propanol	0.148	3.98
2-propanol	0.131	3.52
n-butanol	0.113	3.04
sec-butanol	0.116	3.12
Isobutanol	0.116	3.12
tert-butanol	0.195	5.24
Neopentane	0.112	3.01

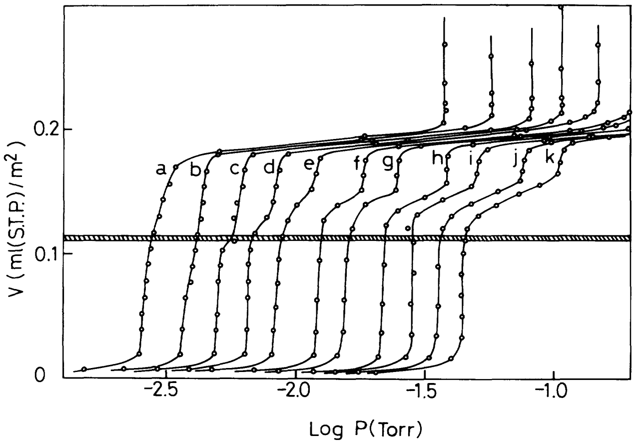

FIG. 2. Adsorption isotherms of *tert*-butanol on graphite: (a) 227.5, (b) 230.1, (c) 232.7, (d) 235.2, (e) 237.8, (f) 240.4, (g) 243.0, (h) 245.5, (i) 248.1, (j) 250.7, and (k) 253.3 K. Shaded area indicates the monolayer capacities of neopentane and the other butanols.

Table I summarizes the saturated amounts of the first adsorbed layer in various alcohols on the exfoliated graphite determined by the *B*-point method [8]. Some of these values are in reasonable agreement with those of area per molecule on graphitized carbon black determined by Avgul *et al.* [9] about 30 years ago. The values for methanol, ethanol, and neopentane were reasonably consistent with the monolayer capacities calculated on the basis of the unit cells of the crystalline monolayer determined by x-ray [7,10] and neutron [11] diffraction, respectively. This confirms that the first adsorbed layers of methanol, ethanol, and neopentane constitute monomolecular-layer-thick films. The saturated amounts of the first adsorbed layer are nearly equal among one group of the branched isomers, except for *tert*-butanol, and decrease in the order methanol>ethanol>propanols >butanols≈neopentane, as expected from their molecular sizes. The saturated amount of the first adsorbed layer for *tert*-butanol is about 1.7 times those for neopentane with an analogous molecular structure and for the other branched isomers of butanol, and increases to the value for ethanol, which is a much smaller molecule. The neutron diffraction study [11] shows that neopentane forms a monolayer of closely packed hexagonal cells, incommensurate with the substrate. The x-ray study [10] also shows that the monolayer of ethanol consists of a closely packed structure of molecules lying flat on graphite. All of these results indicate the unusual nature of molecular packing in the first adsorbed layer of *tert*-butanol.

The x-ray diffraction of the adsorbed phase of *tert*-butanol was measured over the temperature range 30-257 K and the coverage range 0.026-0.180 ml(STP)/m^2. A full account of the results will be described elsewhere. Figure 3 shows the x-ray diffraction pattern measured at a coverage of 0.180 ml(STP)/m^2 and a temperature of 220 K. A numerical method of indexing shows that the 2D lattice parameters are $a = 0.642$ and $b = 1.810$ nm

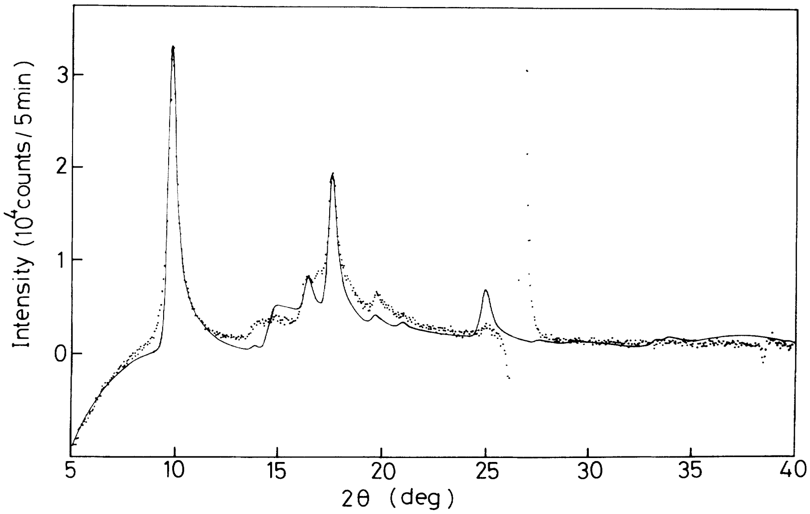

FIG. 3. X-ray diffraction pattern of *tert*-butanol adsorbed on graphite. The features around $2\theta=26°$ come from the imperfect subtraction of the graphite (002) reflection. The solid line represents a fit due to the structure model as described in the text.

with $\beta=94.0°$. This indicates that the film is incommensurate with the graphite surface in its periodicity. A guide to possible structures of a 2D layer can often be obtained by examining the more densely packed planes of the bulk crystal [7,12]. It is known from the literature that there exist several phases in the bulk solid state of *tert*-butanol [13–15]. The crystal structure of only one phase, phase IV, has already been determined at 295 K [15]: space group $P\overline{1}$, $a=0.6393$ nm, $b=0.9481$ nm, $c=1.5126$ nm, $\alpha=85.47°$, $\beta=79.60°$, $\gamma=76.01°$, $z=6$. In this phase, the molecules are arranged in helical chains along the a axis and connected by hydrogen bonds. There are two helices in one unit cell which can be transformed into each other by the inversion center. These two helices are alternately arranged with different heights along the c axis and form a puckered array of the helices in the a-c plane. The diameter of the helix is estimated to be ~0.9 nm from the lattice parameters. The lattice parameter a of our 2D cell coincides with one pitch of the helix and parameter b is about twice the helix diameter. Therefore, we tried to perform a pattern fitting of the whole diffraction pattern on the basis of the model that the two helices having the same helical structure as in the bulk phase are alternately arranged with equal height on the surface. The unit cell contains six molecules. The calculated density (5.18 molecules/nm^2) is almost identical to the density deduced from the adsorption isotherm (5.24 molecules/nm^2) for the first adsorbed lay-

TABLE II. Fractional coordinates of molecules in the 2D unit cell and their z components.

Atom	x	y	z (nm)
C(10)	0.4785	0.2654	−0.2215
O(1)	0.4405	0.2537	−0.0767
C(12)	0.2704	0.2899	−0.2806
C(13)	0.5731	0.1933	−0.2807
C(14)	0.6569	0.3322	−0.2259
C(20)	1.1637	0.3546	0.1734
O(2)	1.1166	0.2926	0.0823
C(22)	0.9612	0.3746	0.2435
C(23)	1.2774	0.4197	0.0906
C(24)	1.3301	0.3224	0.2807
C(30)	0.7815	0.1263	0.1226
O(3)	0.7647	0.2005	0.0603
C(32)	0.5742	0.0785	0.0821
C(33)	0.9865	0.0959	0.0684
C(34)	0.8084	0.1393	0.2768

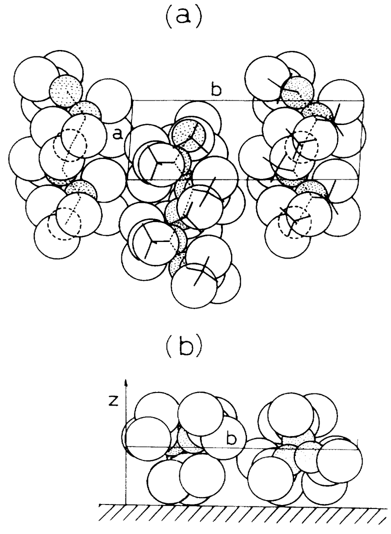

FIG. 4. Probable structure of the bimolecular first layer in *tert*-butanol on graphite: (a) Top view and (b) side view.

er. The 2D structure belongs to the space-group symmetry $p2$ and there are three independent molecules in the cell. However, we assumed the same intermolecular configuration of the three independent molecules as arranged in the a-c plane of the bulk phase IV and reduced the number of the fitting parameters to five: two positional parameters which determine the mutual position of the two helices and three lattice parameters. Also, a thermal factor was not incorporated in the calculation. A powder-averaged Gaussian line shape [16] appropriate to the 2D structure was modified by the usual structure factor expression [17,18] taking into account the z component of the model structure. The profile parameters were used as determined previously on this substrate [19]. As Fig. 3 shows, a good fit between calculated and observed intensities was obtained when the mutual position of the two helices was adjusted along the a and b axes. This proves formation of the helical structure similar to that of the bulk phase in the first adsorbed layer of *tert*-butanol on graphite. The 2D positional parameters determined from the pattern fitting are given in Table II together with their z components relative to the center of the helix. The coordinates of the remaining three molecules are given according to the 3D space-group symmetry $p\bar{1}$ of the bulk phase. The proposed structure model is illustrated in Fig. 4. The molecules are arranged in helical chains along the a axis and connected by hydrogen bonding. One form of the helix rests on two of the three molecules constituting one pitch of the helix while another form of the helix rests on one of the three molecules. This configuration favors lateral interaction between the two helices and leads to a good packing of the helices on the surface. This helical structure constitutes a bimolecular-layer-thick film.

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